

Gas-Liquid Chromatographic Study of Polystyrene-*n*-Alkane Interactions

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ABSTRACT: Gas-liquid chromatography is used to study the thermodynamic interactions between polystyrene and *n*-alkanes (C₆-C₁₀). Polystyrene is used as a stationary phase with *n*-alkanes as the probe molecules. Retention times and specific retention volumes are measured over the temperature interval of 60 to 170°C. Partial molar free energy of mixing, polymer-solvent interaction parameter, glass-transition temperature, and solubility parameter of polystyrene at infinite dilution are calculated. Experimental results are discussed in terms of the theoretical calculations and size of the probe molecules. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 80: 1291-1298, 2001

Key words: gas-liquid chromatography; thermodynamic interactions; polystyrene; retention time; retention volume

INTRODUCTION

Gas-liquid chromatography (GLC) with a polymeric stationary phase has been used to study polymer-solvent interactions.¹⁻⁵ Compared with the conventional techniques,⁶⁻⁸ the method of GLC is more versatile in accurately predicting the thermodynamic interactions in polymer solutions. Other advantages of the GLC method are that it is fast and experiments can be carried out over a wide range of temperature. The present study is undertaken as a part of the sponsored project from the Department of Science and Technology, New Delhi, India, to develop newer techniques to evaluate the thermodynamic interactions between polymers and solvents that have relevance in membrane applications.⁹⁻¹¹ Polystyrene is used as a stationary phase with *n*-hexane, *n*-hep-

tane, *n*-octane, *n*-nonane, and *n*-decane as the probe molecules. From the measured retention times and specific retention volumes, the thermodynamic quantities of interest, that is, partial molar free energy of mixing, polymer-solvent interaction parameter, glass-transition temperature, and solubility parameter of polystyrene at infinite dilution have been calculated. These results are discussed in terms of the interactions between polystyrene and *n*-alkanes.

EXPERIMENTAL

Materials

Polystyrene (number-average molecular mass of 170,000) was received as a gift sample from CI-PET (Mysore, India). The AR grade samples of *n*-hexane, *n*-heptane, *n*-octane, *n*-nonane, and *n*-decane were obtained from S.D. Fine Chemicals (Mumbai, India) and were used without further purification.

Preparation of GLC Column

A [1/8] in. stainless steel column with an inner diameter of 2.1 mm and 2 m length was pur-

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chased from Chrompack Internationals (The Netherlands). The column was first washed with water, then with methanol, and dried completely. It was then washed and blown with dry nitrogen gas. The column nut and back ferrules were fitted onto the column by taking extreme care to avoid any large dead volume of the instrument and weighed to determine the empty weight.

Polystyrene was weighed and dissolved in about 100 mL of chloroform. The polymer sample was then coated carefully onto the inert support. In the actual procedure, the support is piled on a watch glass or a glass dish and a small amount of solution is applied on the top of the support pile. Care was taken to wet the pile as much as possible without letting the solution touch the surface of the dish, either around or under the pile. The solvent was then allowed to evaporate and the pile was thoroughly mixed. Then, a next portion of the solution was applied and the entire procedure was repeated until the solution (including several rinsings of the solution flask) was exhausted. Then the support was dried in an oven and transferred into the column. By this procedure, the amount of polymer is known precisely and the analysis of the column material can be avoided. The column was conditioned overnight using a high-purity nitrogen gas in the gas chromatography at 200°C, and then cooled at the rate of 0.5°C/min to the ambient temperature before each use, to allow the polymer the same thermal history.

The GLC measurements were done on a Purge-Packed HP 6890 Series gas chromatograph (Palo Alto, CA) equipped with a flame-ionization detector (FID). The prepared column was mounted between the inlet and the detector. Dry nitrogen was used as a carrier gas. Flow rate of the carrier gas was measured at room temperature using a soap bubble flow meter and controlled by the column head pressure knob provided with the instrument. The flow rate was monitored frequently by taking an average of three readings every time. These readings usually agreed within 0.5%. The inlet and outlet pressures were frequently monitored. The inlet pressure was generally in the range of 300–450 kPa, whereas the outlet pressure was always atmospheric. Methane gas was used as a marker because it is an inert compound.

The probes were injected using a 5- μ L Hamilton (Hamilton, Reno, NV) syringe. To avoid any artifacts related to overloading of the columns by the probe, we filled the syringe with the probe,

emptied it two to three times and then injected into the column. The air-probe vapor mixture was left in the syringe. Two or three consecutive injections were made for each probe at each set of measurements. The retention times differed by less than 2 s. The positions of peak maxima were obtained from the recorded elution peak from the HP ChemStation software (Product No. G2070AA) supplied with the instrument.

RESULTS AND DISCUSSION

The probe-specific retention volumes V_g^0 corrected to 0°C and zero volume flow rates were calculated using the standard chromatographic relation¹²:

$$V_g^0 = \frac{273.15\Delta t F_{rt} J}{w T_{\text{room}}} \quad (1)$$

where $\Delta t = t_p - t_m$ is the difference between retention times of the probe (t_p) and methane as the marker (t_m); F_{rt} is the volume flow rate of the carrier gas measured at room temperature, T_{room} ; w is the mass of the polymeric stationary phase; and J is a correction factor for gas compressibility, defined by the following relation¹³:

$$J = 3[(P_i/P_o)^2 - 1]/2[(P_i/P_o)^3 - 1] \quad (2)$$

where P_i and P_o are the inlet and outlet pressures, respectively.

The calculated values of V_g^0 , given in Table I, represent the averages of various flow rates and extrapolated to zero flow rate. It is observed that for *n*-hexane, *n*-heptane, and *n*-octane, the results of V_g^0 decrease from 60 to 90°C; again increase continuously up to 140°C; and later decrease slightly up to 170°C. Similarly, for *n*-octane, *n*-nonane, and *n*-decane, the V_g^0 values decrease up to 100°C and then show the same dependencies as those of *n*-hexane, *n*-heptane, and *n*-octane at higher temperatures. The values of V_g^0 increase considerably from *n*-hexane to *n*-decane. A retention diagram of $\log V_g^0$ on $(1/T)$ is shown in Figure 1 for *n*-heptane, *n*-octane, *n*-nonane, and *n*-decane. From this plot, a T_g value of 98.6°C is found for *n*-nonane and *n*-decane, 97.2°C for *n*-octane, and 94.5°C for *n*-heptane, which agrees with the T_g value of polystyrene of around 100°C. However, an increase in T_g with an increase in the chain length of *n*-alkanes results from the plasticizing effect.¹⁴

Table I V_g^0 (cm³/gm) Values for the Probes at Different Temperatures

Temperature (°C)	Hexane	Heptane	Octane	Nonane	Decane
60	1.40	3.74	10.60	23.46	51.83
70	1.87	2.99	6.66	13.84	27.60
80	1.25	2.28	5.15	11.71	24.37
90	0.77	2.17	4.28	9.18	20.00
100	0.98	2.04	3.94	7.31	15.32
110	1.61	3.01	5.40	10.44	22.01
120	2.17	4.91	8.84	16.41	32.33
130	2.52	5.12	9.81	18.86	36.52
140	3.20	6.16	10.99	19.53	26.93
150	3.12	6.45	10.60	19.77	29.69
160	2.84	5.23	8.84	14.58	24.29
170	2.45	4.41	7.46	12.09	18.98

At temperatures below 90°C, the retention time at peak maximum (t_R) is smaller than that observed at peak broadening. A probe sample size of less than 0.05 μ L did not produce convenient peak profiles for the measurement of t_R at infinite dilution of the probe vapors in polystyrene. This may be the result of a decrease in the number of probe molecules eluting in the sharp pulse portion of the peak and their increase in the tail due to the result of a kinetic factor in slow bulk equilibration. Typical peaks for the surface adsorption region are obtained to get the reliable values of t_R using peaks of sufficient height and having larger samples of the probe molecules. This gave an in-

dication of the dependence of t_R on the probe sample size.

The thermodynamic interactions between polystyrene and *n*-alkanes was studied by the calculation of Flory-Huggins interaction parameter, χ at infinite dilution using the following equation^{15,16}:

$$\chi^\infty = \ln\left(\frac{273.15Rv_2}{V_g^0V_1P_1^0}\right) - 1 - (B_{11} - V_1)\frac{P_1^0}{RT} \quad (3)$$

where R is the gas constant, v_2 is the specific volume of polystyrene, V_1 is the molar volume of *n*-alkanes, P_1^0 is the vapor pressure of liquid, B_{11} is the second virial coefficient of *n*-alkanes in the gaseous state, and T is the column temperature; V_1 , P_1^0 , B_{11} , and v_2 were calculated at T . The subscript 1 refers to *n*-alkanes and 2 refers to polystyrene.

The P_1^0 was calculated using the Antoine equation

$$\log P_1^0 = A - \frac{B}{(t + C)} \quad (4)$$

where t is the temperature (in °C), and A , B , and C are the constants taken from the literature.¹⁷ The values of B_{11} were computed using¹⁸:

$$B_{11} = V_c[0.430 - 0.886T_r^{-1} - 0.694T_r^{-2} - 0.0375(20\omega - 1)T_r^{-5}] \quad (5)$$

where V_c is the critical molar volume, $T_r = T/T_c$ is the reduced temperature, T_c is the critical tem-

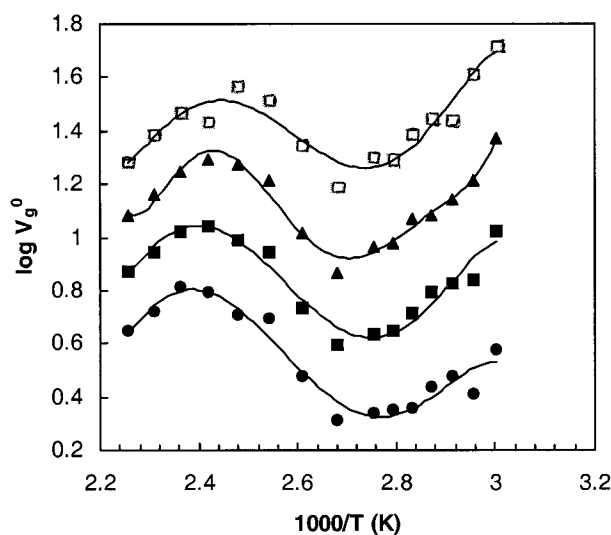


Figure 1 Retention diagram of $\log V_g^0$ versus $1/T$ for (●) *n*-heptane, (■) *n*-octane, (▲) *n*-nonane, and (□) *n*-decane.

Table II The χ Values for the Probes at Different Temperatures

Temperature (°C)	Hexane	Heptane	Octane	Nonane	Decane
60	4.03	3.93	3.76	3.85	3.93
70	3.43	3.78	3.81	3.91	4.05
80	3.53	3.71	3.68	3.64	3.69
90	3.24	2.87	2.86	2.76	2.70
100	3.23	3.21	3.25	3.34	3.30
110	2.50	2.54	2.63	2.63	2.55
120	1.98	1.79	1.84	1.85	1.80
130	1.62	1.51	1.46	1.40	1.34
140	1.18	1.10	1.09	1.08	1.33
150	1.03	0.84	0.88	0.91	0.93
160	0.95	0.85	0.84	0.85	0.85
170	0.94	0.83	0.80	0.80	0.84

perature, and ω is the accentric factor of the solvents. The values of these parameters were taken from the literature.^{19,20}

The calculated values of χ presented in Table II decrease with an increase in temperature for all the probes, but no systematic dependence of χ on

the size of the probe molecules is observed. The decrease in χ with increasing temperature is attributed to an increased segmental movement of polystyrene at higher temperatures, thus creating extra free volume with which the probe can interact. At lower temperatures, bulk adsorption

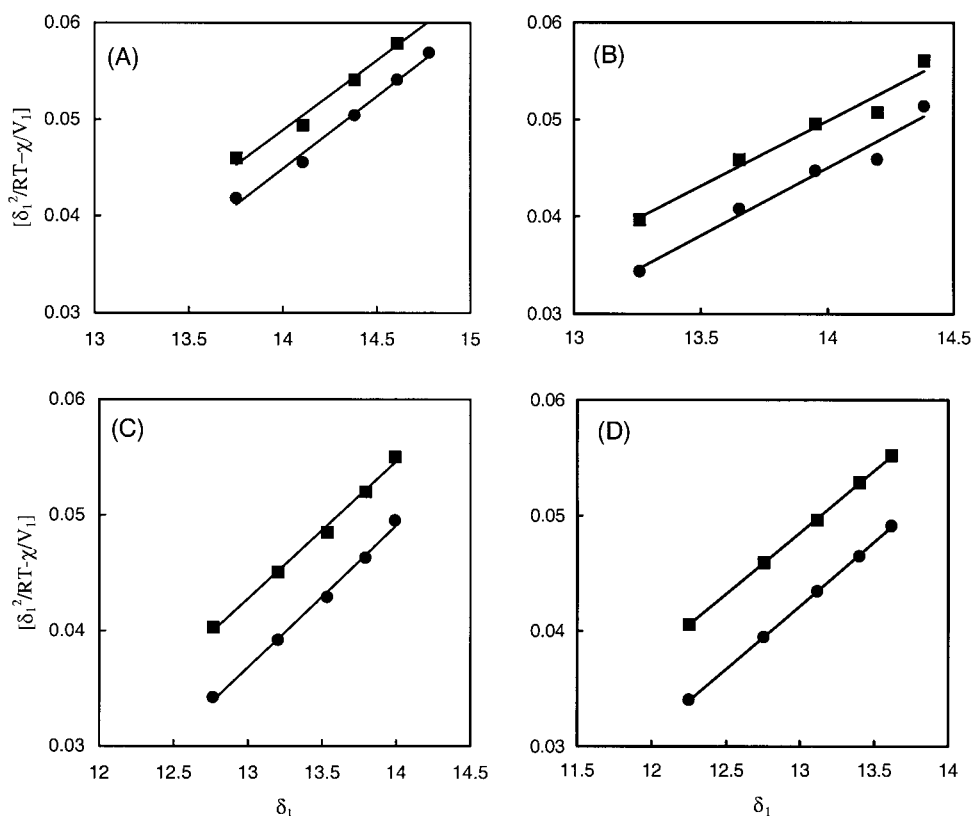


Figure 2 $[(\delta_1^2/RT) - (\chi/V_1)]$ versus δ_1 where (●) for δ_1 is calculated using eq. (10) and (■) for δ_1 calculated using eq. (13) at (A) 70°C, (B) 90°C, (C) 110°C, and (D) 130°C.

Table III Solubility Parameter δ_P Values for the Probes at Different Temperatures

Temperature (°C)	δ_P (cal/cm ³) ^{1/2}					
	From Eq. (7)					
	For δ_i from Eq. (10)		For δ_i from Eq. (13)		From Eq. (18)	
	Slope	Intercept	Slope	Intercept	Slope	Intercept
60	13.95	12.77	14.60	13.21	14.43	16.72
70	10.43	10.59	10.93	10.98	12.48	13.13
80	11.70	11.38	12.28	11.91	12.11	12.85
90	10.34	10.44	10.96	10.93	12.24	12.91
100	10.97	10.46	11.55	11.24	12.37	13.30
110	9.68	9.68	10.27	10.25	11.49	12.02
120	9.28	9.28	9.96	9.87	11.09	11.63
130	9.00	8.98	9.70	9.58	10.76	11.26
140	7.36	7.62	7.91	8.13	9.57	9.52
150	7.35	7.53	7.92	8.07	9.40	9.39
160	7.12	7.32	7.70	7.86	9.14	9.05
170	6.96	7.15	7.54	7.70	8.90	8.75

of the probes might have taken place, leading to an increased interaction between probe molecules and polystyrene.

Flory theory was combined with the Hildebrand solubility theory²¹ to calculate the solubility parameter, δ_2 of the polymer from χ using:

$$\chi = \left(\frac{V_1(\delta_1 - \delta_2)^2}{RT} \right) \quad (6)$$

The solubility parameter δ_1 of the solvent can be easily measured, but that of the polymer, δ_2 , is obtained indirectly. The value of δ_2 when calculated from eq. (6) was often found to be inaccurate

and hence, the approach of DiPaola-Baranyi and Guillet¹⁸ was used to compute δ_2 as

$$[(\delta_1^2/RT) - (\chi/V_1)] = (2\delta_2/RT)\delta_1 - \delta_2^2/RT \quad (7)$$

This equation allows a combination of data for all the probes measured by plotting the experimental left-hand side versus δ_1 . The plot shown in Figure 2 is a straight line and δ_2 is calculated from the slope and the intercept.

Because the interaction parameter has the free energy characteristics, eqs. (6) and (7) can be replaced by eqs. (8) and (9) as

Table IV Free Energy of Mixing $\Delta\bar{G}_1^\infty$ (cal/mol) for the Probes at Different Temperatures

Temperature (°C)	Hexane	Heptane	Octane	Nonane	Decane
60	3657.1	3561.2	3428.2	3469.7	3512.9
70	3357.4	3573.1	3568.2	3619.2	3698.8
80	3532.5	3630.9	3584.4	3542.1	3561.4
90	3562.8	3476.4	3541.3	3922.8	3576.4
100	3523.7	3471.6	3479.2	3522.0	3476.3
110	3064.4	3059.9	3097.3	3081.6	3002.7
120	2740.8	2560.6	2568.3	2556.9	2501.7
130	2528.5	2402.4	2333.6	2268.3	2199.7
140	2241.0	2127.9	2091.4	2062.9	2246.4
150	2167.0	1966.3	1973.0	1968.5	1971.1
160	2157.5	2026.3	1984.6	1969.6	1951.9
170	2202.1	2061.6	1996.1	1973.0	1984.4

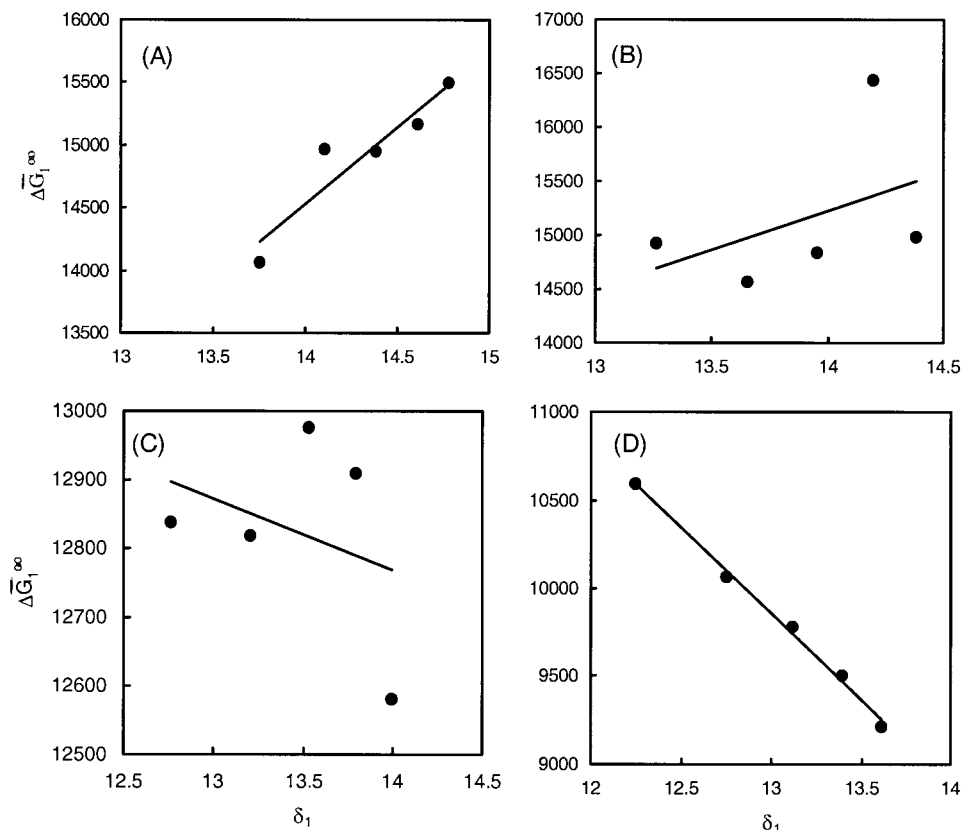


Figure 3 $\Delta\overline{G}_1^\infty$ versus δ_1 at (A) 70°C, (B) 90°C, (C) 110°C, and (D) 130°C.

$$\chi = \left(\frac{V_1(\delta_1 - \delta_2)^2}{RT} \right) + \chi_s \quad (8)$$

and

$$[(\delta_1^2/RT) - (\chi/V_1)] = (2\delta_2/RT)\delta_1 - [(\delta_2^2/RT) + (\chi_s/V_1)] \quad (9)$$

Thus, the entropic contribution, χ_s to χ can be computed.

Fundamentally, the solubility parameter δ_i of a liquid is defined as the square root of cohesive energy density for a unit volume of the liquid. The δ_1 for the liquid required in the calculation of δ_2 of the polymer is calculated as²¹

$$\delta_i = \left(\frac{E_{\text{coh}}}{V_i} \right)^{1/2} = \left(\frac{\Delta H_V - RT}{V_i} \right)^{1/2} \quad (10)$$

The cohesive energy density of the probe at the column temperature was calculated using¹⁸

$$E_{\text{coh}} = 9.4062RT_c \exp(1.0582\omega) \times \exp(-1.0655T_r^{12} - 0.5553T_r^{12}) \quad (11)$$

where T_c is the critical temperature of the probe, $T_r (= T/T_c)$ is the reduced temperature, and ω is the acentric factor of the solvents. These data were taken from the literature.^{19,20} To compute the molar volume of the probe, its density d_t at the column temperature t is required, which was calculated using

$$d_t = \frac{d_{\text{ref}}}{\alpha(t - t_{\text{ref}}) + 1} \quad (12)$$

Here, t_{ref} is the reference temperature, d_{ref} is the probe density at the reference temperature, and α is the thermal expansion coefficient of the probe taken from the literature.²² The value of d_t was then used to compute V_i of eq. (10).

Alternatively, the solubility parameter of the probe was calculated using¹⁹

$$\frac{\delta_1^2}{f_1^2} = \sigma_1(W_1^2 + P_1^2 + A_1D_1) \quad (13)$$

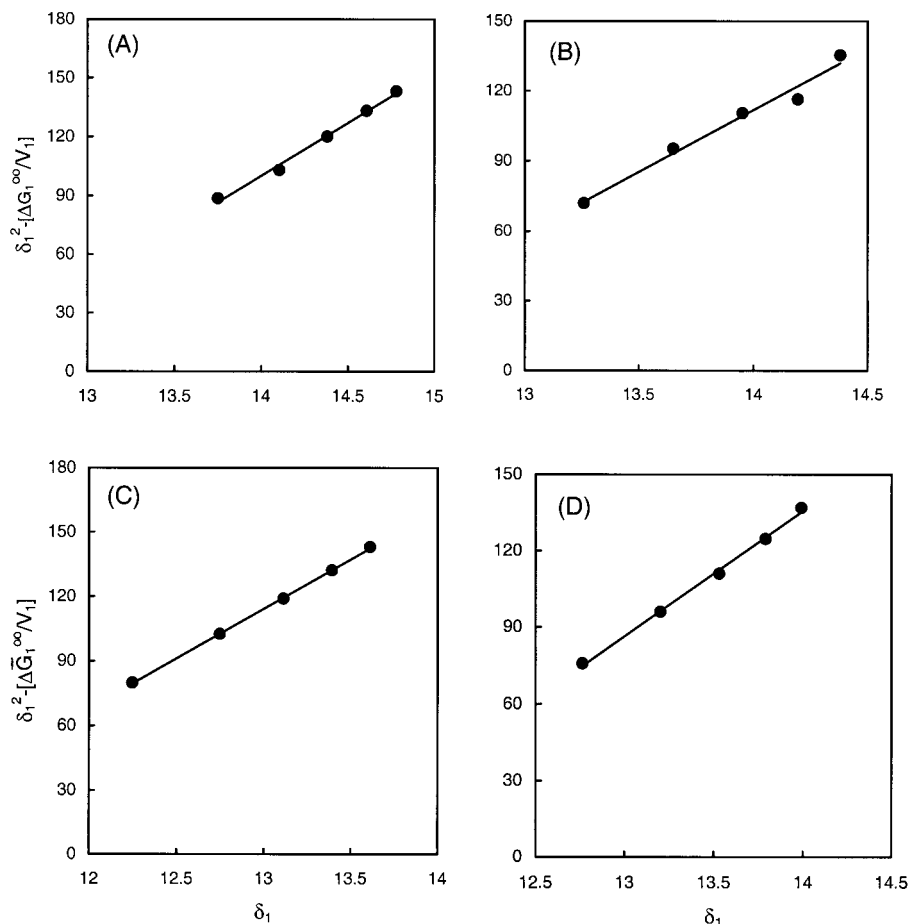


Figure 4 $[(\delta_1^2 - (\Delta\bar{G}_1^\infty/V_1))$ versus δ_1 at (A) 70°C, (B) 90°C, (C) 110°C, and (D) 130°C.

Here, the parameters σ_1 , W_1 , P_1 , A_1 , and D_1 were taken from the literature¹⁹; the quantity f_1 is the temperature-dependent cohesive energy density factor, which was calculated as

$$f = \exp(0.5328[T_{r,\text{ref}} - T_r] + 0.2777[T_{r,\text{ref}}^{12} - T_r^{12}]) \quad (14)$$

where $T_{r,\text{ref}}$ and T_r are the reduced temperatures at reference temperature (i.e., 25°C) and at the column temperature, respectively.

The solubility parameter of polystyrene was then determined by plotting the values of $(\delta_1^2/RT) - (\chi/V_i)$ versus δ_i using eq. (7). A representative plot is shown in Figure 2 at 70, 90, 110, and 130°C. From slope and intercept of the straight lines, δ_p was calculated. These data are given in Table III. It is observed that δ_2 is about 9.2 (cal/cm³)^{1/2} at 130°C, which is in good agreement with the expected value of 9.0 to 10.4 (cal/cm³)^{1/2} from the literature.¹⁸

Partial molar free energy of sorption $\Delta\bar{G}_1^\infty$ was calculated using

$$\Delta\bar{G}_1^\infty = RT \log\left(\frac{RT_0}{V_g^0 P_1^0 M_1}\right) - \frac{P_1^0}{RT} (B_{11} - V_1) \quad (15)$$

where T_0 is the absolute temperature in Kelvin (=273.15°C). These results are summarized in Table IV. However, according to Hildebrand and Scott,²¹ the energy of mixing ΔE_m of two liquids at constant volume is given by

$$\frac{\Delta E_m}{\phi_1 \phi_2} = V_m (\delta_1 - \delta_2)^2 \quad (16)$$

Here, ϕ_1 and ϕ_2 are the volume fractions of the components, V_m is the average molar volume based on mole fractions, and δ_1 and δ_2 refer to the solubility parameter of each component. Knowing the interaction parameter, molar volume, and sol-

ubility parameter of the probes at the column temperature, the solubility parameter of the polymer can be determined. The term ΔE_m is substituted by the energy at constant pressure (i.e., the free energy), which is approximately the same and thus eq. (16) takes the form

$$\Delta \bar{G}_1^\infty = V_1(\delta_1 - \delta_2)^2 \quad (17)$$

When the free-energy change is zero, then $\delta_1 = \delta_2$. A plot of partial molar free energy of mixing $\Delta \bar{G}_1^\infty$ versus δ_1 , as shown in Figure 3, gave δ_2 when extrapolated to $\Delta \bar{G}_1^\infty = 0$. For comparison, eq. (17) can be rewritten as

$$\delta_1^2 - (\Delta \bar{G}_1^\infty/V_1) = (2\delta_2)\delta_1 - \delta_1^2 \quad (18)$$

The results of $[\delta_1^2 - \Delta \bar{G}_1^\infty/V_1]$ versus δ_1 are presented in Figure 4. The slopes and intercepts of the lines were calculated by the least-squares procedures. The resulting values of δ_2 are compared in Table III.

CONCLUSIONS

Thermodynamic interactions between polystyrene and *n*-alkanes are studied using a gas-liquid chromatographic technique. The values of Flory-Huggins interaction parameter evaluated by this method are used to understand the polymer-solvent interactions. The determination of the polymer solubility parameter was possible, giving further evidence of the applicability of the method on a routine basis. The observed T_g values are in good agreement for higher alkanes than those for lower alkanes. The solubility parameter values of polystyrene at different temperatures agree with the literature data at the temperatures above the T_g of the polymer. At higher temperatures, the interaction of the probe with the polymer becomes higher. The solubility parameters calculated by

using the free energy of mixing are slightly different when compared to the expected values.

REFERENCES

1. Bruan, J. M.; Guillet, J. E. *Macromolecules* 1975, 8, 882.
2. Galin, M. *Macromolecules* 1989, 10, 1239.
3. Oner, M.; Dinger, S. *Polymer* 1987, 28, 279.
4. Kaya, I.; Demirelli, K. *Polymer* 2000, 41, 2855.
5. Kikic, I.; Alessi, P.; Cortesi, A. *Fluid Phase Equilib* 2000, 169, 117.
6. Aminabhavi, T. M.; Munk, P. *Macromolecules* 1979, 12, 607.
7. Aminabhavi, T. M.; Munk, P. *Macromolecules* 1979, 12, 1186.
8. Aminabhavi, T. M.; Munk, P. *Macromolecules* 1979, 12, 1194.
9. Baker, R. W. *Membrane Technology and Applications*; McGraw-Hill: New York, 2000.
10. Aminabhavi, T. M.; Khinnavar, R. S.; Harogoppad, S. B.; Aithal, U. S.; Nguyen, Q. T.; Hansen, K. C. *J Macromol Sci Rev Macromol Chem Phys* 1994, C34, 139.
11. Aminabhavi, T. M.; Harogoppad, S. B.; Khinnavar, R. S.; Balundgi, R. H. *J Macromol Sci Rev Macromol Chem Phys* 1991, C31, 433.
12. Littlewood, A. B.; Phillips, C. S. G.; Price, D. T. *J Chem Soc* 1955, 1480.
13. Cruikshank, A. J. B.; Windser, M. L.; Young, C. L. *Proc R Soc London Ser A* 1966, 295, 259, 271.
14. Shobha, H. K.; Kishore, K. *Macromolecules* 1992, 25, 6755.
15. Flory, P. J. *J Chem Phys* 1941, 9, 660.
16. Huggins, M. L. *J Chem Phys* 1941, 9, 440.
17. Yaws, C. L.; Yang, H. C. *Hydrocarbon Process* 1989, October, 65.
18. DiPaola-Baranyi, G.; Guillet, J. E. *Macromolecules* 1978, 11, 228.
19. Tian, M.; Munk, P. *J Solution Chem* 1995, 24, 267.
20. Yaws, C. L.; Chen, D.; Yang, H.-C.; Tan, L.; Nico, D. *Hydrocarbon Process* 1989, July, 61.
21. Hildebrand, J. H.; Scott, R. L. *The Solubility of Non-Electrolytes*, 3rd ed.; Dover Publications: New York, 1964.
22. Riddick, A. R.; Bunger, W. B.; Sakano, T. K. *Organic Solvents, Techniques of Chemistry, Vol. II*; Wiley-Interscience: New York, 1986.